

Thermoplastic Starch

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Introduction

Ever-increasing interest in the utilization of renewable materials has driven researchers to intensively study and develop biodegradable plastics. Compared to protein and lipid, starch has become one of the most promising materials for use in manufacturing plastics, due to its biodegradability, universality, renewability, and low cost (Wilhelm et al., 2003). The most significant sources of starch are cereal grains, such as corn, wheat, and rice, as well as tubers, such as potato and cassava. Native starch exists in a semicrystalline granule and is comprised of two major polysaccharides: amylose and amylopectin. Amylose consists of α -(1-4)-linked D-glucose and amylopectin has the same backbone as amylose but with myriad α -(1-6)-linked branch points. These two polysaccharides are the polymer sources used in the production of biodegradable plastics. Native starch does not

have thermoplastic properties; however, with the addition of plasticizers, thermal processes, and shear stress, native starch gelatinizes and reveals its thermoplastic character. Thermoplastic starch (TPS) can be molded into different products with various shapes, or blown into films. The properties of these products, such as tensile strength (TS), elongation at break (E), elastic modulus (EM), glass transition, gas barrier, and others are significantly affected by the processing parameters, plasticizer content, moisture content, etc. Starch-based polymers have a variety of industrial uses, such as for food packaging, flexible films, injection-molded pots, candy trays, compost bags, plant pots, coatings, drug-delivery capsules, golf tees, cutlery, plates, and food containers (Stepito, 2003). Starch-based polymers have two significant shortcomings: high water sensitivity and low mechanical strength. Recent research has focused on overcoming these two problems by, for example, blending starch with other polymers, adding nanoclay in the starch matrix, choosing different kinds of plasticizer, and using starch sources with high amylose content. This chapter reviews the latest developments aimed at improving TPS properties.

TPS Manufacturing process: casting methods and extrusion procedures

Thermoplastic starch can be obtained by utilizing casting solutions or extrusion procedures. In the casting solution method, starch, plasticizer, and other additives are first formulated into a water suspension, which is subject to heating during which the starch granule is gelatinized. The heated suspension is cast into a well-leveled platform, cooled down and dried until a starch film can be peeled from the platform. The casting solution procedure is illustrated in Figure 16.1. During the casting procedure, heating temperature and time can significantly affect the TPS. Koch et al. (2010) reported that heating for 5 to 15 minutes at 130 to 150°C resulted in starch degradation and fragmented TPS films. The heating temperature exhibited a greater effect on starch degradation than did the heating time.

The casting method is commonly used in labs to study the starch gelatinization, plasticization, and thermomechanical properties of the TPS film, but it is not practical for industry-scale production. For large-scale manufacture, an extrusion process is used. A typical single-screw extruder consists of a hopper, barrel, feed screw, thermocouples, and dies (Figure 16.2). Moscicke et al. (2012) prepared starch pellets or beads (also referred to as resin for plastic) by feeding the raw materials (e.g., starch and glycerol) into a single-screw extruder. The extrudates were then chopped with a high-speed cutter into pellets of around 5 mm in length (Figure 16.3). During the extrusion process, thermal process and shear stress destroy starch crystallinity, leading to formation of a continuous amorphous mass. Water contained in the starch and other plasticizers interacts with the starch through hydroxyl bonding. The starch undergoes fragmentation, melting and

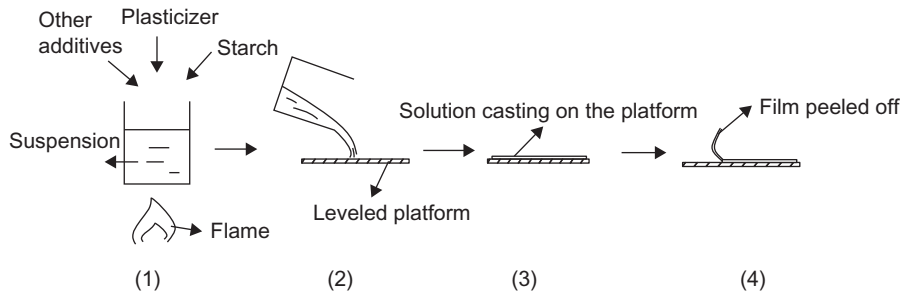


FIGURE 16.1

Suspension casting procedure to make TPS film: (1) Starch suspension formulation and heating. (2) Casting the suspension onto a platform. (3) Cooling and drying. (4) Peeling the dried film off of the platform.

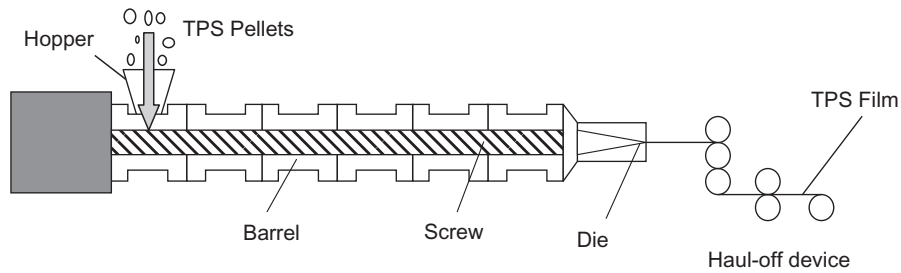


FIGURE 16.2

A schedule of a typical extruder and extrusion processing.

Adapted from Li et al., 2011.

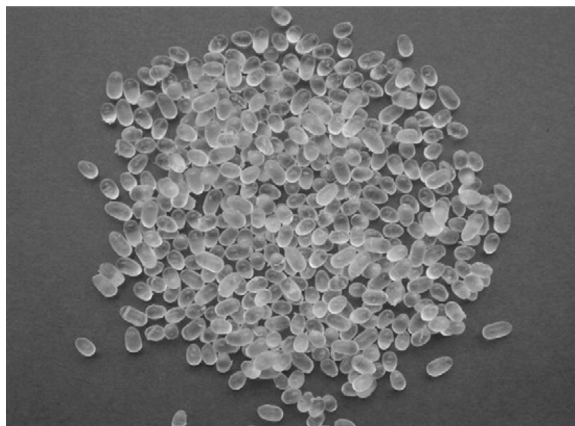


FIGURE 16.3

Pellets of potato starch containing 25% glycerol.

From Moscicke et al., 2012.

**FIGURE 16.4**

TPS film blowing.

From Moscicke et al., 2012.

flowing like synthetic polymers (Pushpadass and Hanna, 2009). The starch pellets are then formulated with various additives, such as synthetic polymer or nanoclay, and fed again into the extruder from the hopper along the feed screw through the barrel chamber. The starch pellets homogeneously melt and mix with the additives, and travel further to the die of the screw. The die is precisely machined with a pattern opening such that the extruded starch mix takes the die pattern for its cross-sectional area. TPS extrudates from the die solidify quickly. Before solidifying, TPS extrudates can be blown into films or sheets or molded into desired shapes (Thunwall et al., 2006a,b). Moscicke et al. (2012) achieved TPS film blowing based on the single extruder shown in Figure 16.4.

Melo et al. (2011) compared the effect of casting method and extrusion process on the properties of TPS films. They concluded that cast films were transparent, homogeneous, and smooth, whereas extruded films were opaque. Also, the cast films presented significant lower water vapor permeability (WVP) values and higher stress-at-break values than extruded films.

Improvements in TPS properties

Rindlav-Westling et al. (1998) reported that TPS film exhibits excellent oxygen barrier properties comparable with typical packaging plastics, such as low-density

Table 16.1 Mechanical Properties of TPS Made from Various Starch Types

TPS Product Formulation	TS (MPa)	E (%)	EM (MPa)	References
Rice starch film with glycerol	1.6–11	3–60	21–533	Dias et al. (2011)
Rice starch film with sorbitol	11–22	3–4	456–1053	Dias et al. (2011)
Cassava starch with glycerol	1.4–1.6	83–101	11–21	Muller et al. (2009a)
Corn starch with glycerol and stearic acid	0.2–2.9	46–91	3–38	Pushpadass and Hanna (2009)
Corn starch films	0.9–4.8	—	—	Da Roz et al. (2006)
Potato starch with glycerol	3	47	45	Thunwall et al. (2006a,b)
Corn starch with glycerol	3	20	NA	Dai et al. (2008)
Rice starch with glycerol	3.2	—	—	Mehyar and Han (2004)
Pea starch with glycerol	4.2	—	—	Mehyar and Han (2004)
Pea Starch with glycerol	1.4–5.8	38–51	8–98	Zhang and Han (2006a,b)

Abbreviations: *E*, elongation at break; *EM*, elastic modulus; *TPS*, thermoplastic starch; *TS*, tensile strength.
Source: Adapted from Zhang et al. (2008).

polyethylene (LDPE) and ethyl vinyl alcohol (EVOH). As mentioned above, however, TPS products tend to be very sensitive to moisture and show low mechanical properties. Table 16.1 and Table 16.2 list the tensile properties and water vapor permeability for some TPS products made from native starch. From the tables, it can be seen that tensile strength (TS) is typically less than 5 MPa, elongation at break (E) less than 50%, and water vapor permeability (WVP) up to $31.2 \text{ g mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$. These major shortcomings have limited the wide application of TPS in industry. In order to mediate these two disadvantages, several methods have been developed to enhance TPS properties, including selecting starch sources with a higher amylose content, using more efficient plasticizers, adding nanoclay or fiber, and blending starch sources with either biodegradable or nonbiodegradable polymers.

Starch sources

Thermoplastic starch composites utilizing native starch derived from diverse botanical source have been widely studied. These studies demonstrate that

Table 16.2 Comparison of Water Vapor Permeability (WVP) Values of TPS Films

TPS Formulation	WVP (g mm m ⁻² h ⁻¹ kPa ⁻¹)	References
Rice starch with glycerol	16.7–31.2	Dias et al. (2011)
Rice starch with sorbitol	9.6–10.9	Dias et al. (2011)
Corn starch with glycerol	12.0–20.0	Pushpadass and Hanna (2009)
Cassava starch with glycerol	2.33–10.3	Muller et al. (2009a)
Yam starch with glycerol	0.34–0.65	Mali et al. (2002)
Corn starch with glycerol	1.93–2.41	Mali et al. (2006)
Cassava starch with glycerol	1.45–2.25	Mali et al. (2006)
Pea starch with glycerol	2.75–9.97	Zhang and Han (2006a)
Pea starch with sorbitol	2.61–6.70	Zhang and Han (2006a)
Pea starch with fructose	1.96–4.78	Zhang and Han (2006a)
Pea starch with mannose	2.27–4.63	Zhang and Han (2006a)
Corn starch with sorbitol	0.63	Garcia et al. (2000)

Source: Adapted from Zhang et al. (2008).

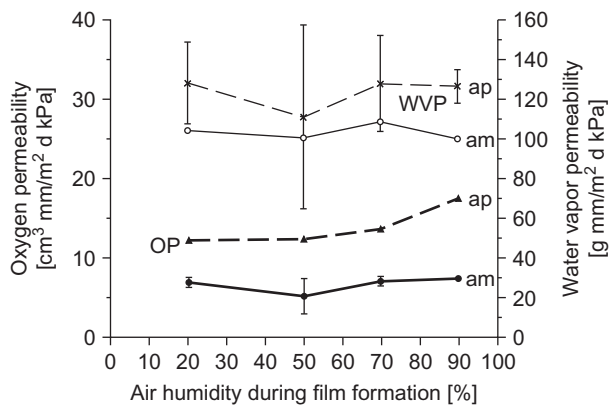
starches from different botanical sources have different amylose/amylopectin ratios, which allow development of biodegradable TPS films with different mechanical properties (Rindlav-Westling et al., 1998). Lopez and Garcia (2012) reported that starches from ahipa, cassava, and corn, containing 1.6%, 15.5%, and 23.9% amylose, respectively, demonstrated good film-forming capacity. The starch film made of corn starch, which contained more amylose, was more moisture resistant and less flexible than the ahipa and cassava starch films. Phan et al. (2005) reported that cassava, normal rice, and waxy rice starch contained 26.78%, 19.50%, and 3.64% amylose, respectively. The films made of cassava starch were stronger and more water resistant than others. Table 16.3 summarizes these findings.

Muscat et al. (2012) also studied the effect of the amylose content of starch on the TPS films. Two kinds of corn starches were investigated; one contained 25% amylose and the other 80% amylose. They reported that films with high amylose content showed higher TS and EM values and lower E values than low-amylose starch films. Myllarinen et al. (2002) attributed this difference to the different sensitivities of amylose and amylopectin to the plasticizers. They stated that the amylose was less susceptible to the plasticizing effect than amylopectin. Plasticizer would improve the film's flexibility and extensibility to a great extent when the film contained more amylopectin. Lopez and Garcia (2012) studied the thermomechanical properties of ahipa, cassava, and corn starch films. They reported that plasticizer molecules interacted more effectively with ahipa starch, which contains more amylopectin than do cassava and corn starches, due to the higher rate of hydrogen bonding. In addition, amylose was reported to affect the

Table 16.3 Mechanical Properties and Water Vapor Permeability of Various Starch Sources

Starch Source	Amylose Content (%)	TS (MPa)	E (%)	WVP ($10^{-11} \text{ g}^{-1} \text{ m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$)	References
Cassava	26.78	35.17	2.64	11.22	Phan et al. (2005)
Normal rice	19.50	28.85	2.01	16.75	Phan et al. (2005)
Waxy rice	3.64	8.51	0.72	21.03	Phan et al. (2005)
Corn	23.9	31.8	4.1	12	Lopez and Garcia (2012)
Cassava	15.5	3.8	28.9	14	Lopez and Garcia (2012)
Ahipa	11.6	4.7	21.8	16	Lopez and Garcia (2012)

Abbreviations: *E*, elongation at break; *TPS*, thermoplastic starch; *TS*, tensile strength; *WVP*, water vapor permeability.

**FIGURE 16.5**

Oxygen permeability (OP) and water vapor permeability (WVP) of amylose (am) and amylopectin (ap) films.

From Rindlav-Westling et al., 1998.

gas barrier properties of TPS films. Figure 16.5 shows the oxygen permeability (OP) and WVP of amylose film and amylopectin film at a wide range of relative humidities and indicates that both OP and WVP are higher for the amylopectin films than for the amylose films. Phan et al. (2005) reported that the WVP of films is directly proportional to the amylopectin content (Figure 16.6). They suggested that amylose polymers recrystallized into a B-type crystalline structure,

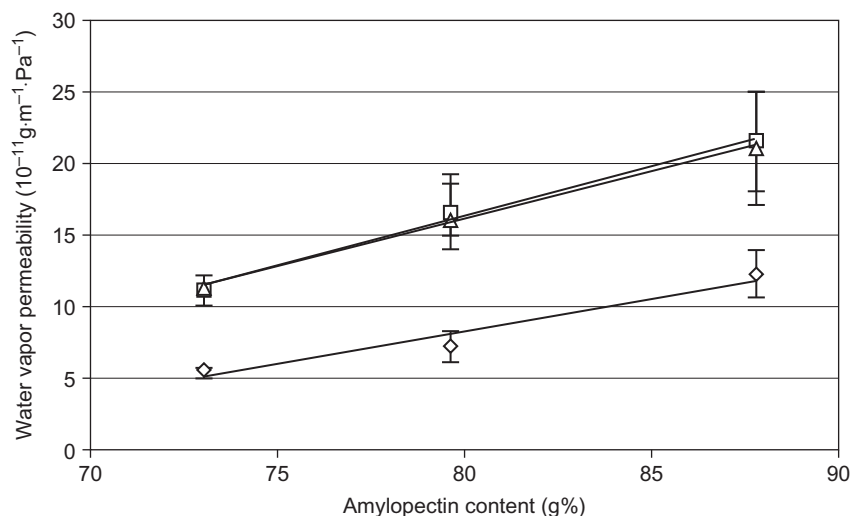


FIGURE 16.6

Water vapor permeability (WVP) is directly proportional to the amylopectin content in starch-based films (Δ: permeability at ΔRH: 99-22%; □: permeability at Δ RH: 84-22%; ◇: permeability at Δ RH: 57-22%).

From Phan et al., 2005.

whereas amylopectin chains were completely amorphous. Diffusion of moisture is easier in amorphous systems than in crystalline ones.

Plasticizer

McHugh et al. (1993) observed that plasticizers are nonvolatile substances with high boiling points without phase separation from polymers; they change the mechanical and thermal properties of polymeric materials when they are added to the polymer matrix. Without the presence of plasticizers, native starch is not considered a thermoplastic polymer (Ma et al., 2007). In the presence of plasticizers (e.g., water, glycerol, sorbitol) at high temperatures (90 to 180°C) and under shear, native starch readily melts and flows, allowing for its use as an extrusion, injection molding, or blowing material, similar to most conventional synthetic thermoplastic polymers (Ma et al., 2007). The role of plasticizers is to decrease the inherent brittleness of starch by reducing the intermolecular forces between starch chains, decreasing the glass transition temperature, increasing the flexibility of films, and lowering the melting temperature of starch below its decomposition temperature (230°C) (Ke and Sun, 2001; Souza and Andrade, 2002; Stepto, 2003). Thanks to plasticizers, native starch can be turned into thermoplastic starch.

The main plasticizers that have been successfully employed in TPS compositions include water, glycerol, ethylene glycol, sorbitol, sucrose, fructose, glucose, urea, amides, and amino acids (Abdorreza et al., 2011; Da Roz et al., 2006; Galdeano et al., 2009; Lourdin et al., 1997; Pushpadass et al., 2008; Smits et al., 2003; Stepto, 2003; Zhang and Han, 2006a,b). Water is considered one of the most effective plasticizers due to its small size, ease of insertion, and positioning within the three-dimensional starch networks. Zhang and Han (2006a) compared the plasticization effect of glycerol, sorbitol, and monosaccharides on starch films and reported that glycerol-plasticized films had lower glass transition temperatures (T_g), around -70°C , indicating that glycerol had a greater plasticization effect on the starch films. Galdeano et al. (2009) compared the effects of glycerol and sorbitol on the moisture content of starch films and found glycerol-plasticized starch films adsorbed water from air faster and in a greater amount. Zhang and Han (2006a) reported similar results for moisture content and attributed the higher moisture content in glycerol-plasticized starch film to the higher polarity of glycerol, which has dielectric constant of 42.5 at 25°C , while sorbitol has the dielectric constant of 33.5 at 80°C .

Abdorreza et al. (2011) investigated the effects of glycerol and sorbitol on the heat sealability of the starch films and found that sorbitol-plasticized films exhibited significantly better heat sealability than did the glycerol type. Zhang and Han (2006a,b) noted that fructose-, glucose-, and mannose-plasticized TPS films had significantly higher TS and E, lower WVP, and similar EM compared to glycerol- or sorbitol-plasticized films, suggesting that monosaccharides could be better plasticizers in terms of physical properties of the starch films. They also observed that glycerol provided lower T_g values and required less apparent activation energy (H_a , in kJ/mol) for starch films to go through glass transition, whereas glucose-plasticized films required greater H_a . Urea, formamide, ethanolamine, and ethylenebisformamide, which contain $-\text{CO}-\text{NH}-$ functional groups, also proved to be efficient plasticizers (Huang et al., 2006; Ma and Yu, 2004; Wang et al., 2008; Yang et al., 2006a,b). Zullo and Iannace (2009) reported that urea/formamide mixtures worked more effectively as plasticizers than glycerol in making homogeneous and robust TPS films. Ma and Yu (2004) calculated the hydrogen bond energy for urea–starch, formamide–starch, acetamide–starch, and glycerol–starch composites and reported the strength of these hydrogen bonding as follows: urea > formamide > acetamide > polyols. Consequently, they attributed the greater effectiveness of urea, formamide, and acetamide in plasticizing TPS to the stronger hydrogen bonding between $-\text{CO}-\text{NH}-$ groups of urea, formamide, acetamide, and HO-groups of starch. However, due to food safety concerns, amide groups containing plasticizers are not recommended for use in food packaging and edible films (Yu et al., 2010). Adhikari et al. (2010) compared the plasticization effect of glycerol and xylitol to each other on the starch films. They found that xylitol was a more effective plasticizer due to its relatively larger molecular size and tendency to form stronger hydrogen bonds with starch molecules compared to glycerol.

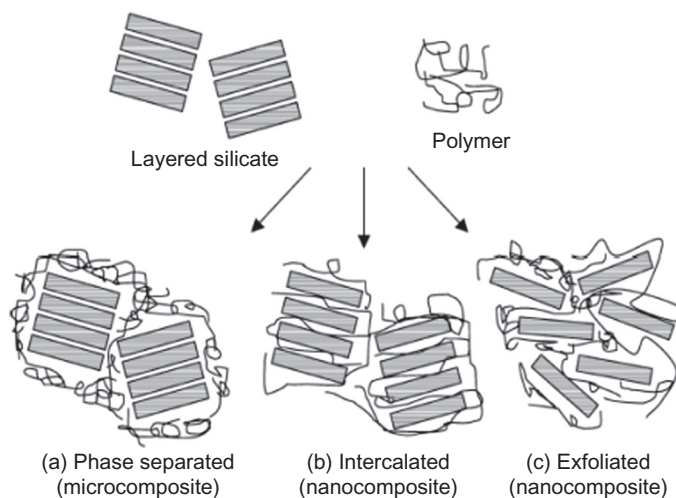


FIGURE 16.7

Three types of nanocomposite structure of polymer-layered silicate clay materials.

From McGlashan and Halley, 2003.

Nanoclay

Nanoclay has been blended with TPS to improve TPS properties, including mechanical properties, thermal stability, and water resistance (Chivrac et al., 2009; Chung et al., 2010; Cyras et al., 2008; de Carvalho et al., 2001; Wu, et al., 2009). The main reason for such improvement is the large interface area between nanoclay and starch, which results in a large number of interactions between the starch molecules and the nanofillers (Aouada et al., 2011; Chung et al., 2010). For montmorillonite (MMT) nanoclay, this area may attain 600 to 800 m²/g when the nanofiller is homogeneously dispersed (Chivrac et al., 2009). Tactoid, intercalated, and exfoliated nanocomposite structures were studied by McGlashan and Halley (2003) (Figure 16.7). Only the intercalated and exfoliated structures of nanocomposites were considered to be homogeneous dispersions, which can efficiently improve the physical and mechanical properties of TPS. Dispersion of the nanoclay in the starch matrix is commonly determined by x-ray diffraction (XRD) and transmission electron microscopy (TEM) (Namazi et al., 2012). Figure 16.8 shows the XRD patterns for potato starch, MMT and their nanocomposites (Cyras et al., 2008). MMT showed a single 001 diffraction peak at low 2θ angles (7.3°), while starch presented no peak in the study range. In the composite films, the 001 diffraction peak of the MMT (7.3°) was shifted to a lower angle (4.9°) regardless of the clay content. These results indicate that either the glycerol or the polymer chains or both entered into the silicate layers, forming intercalated starch/MMT nanocomposites. Chivrac

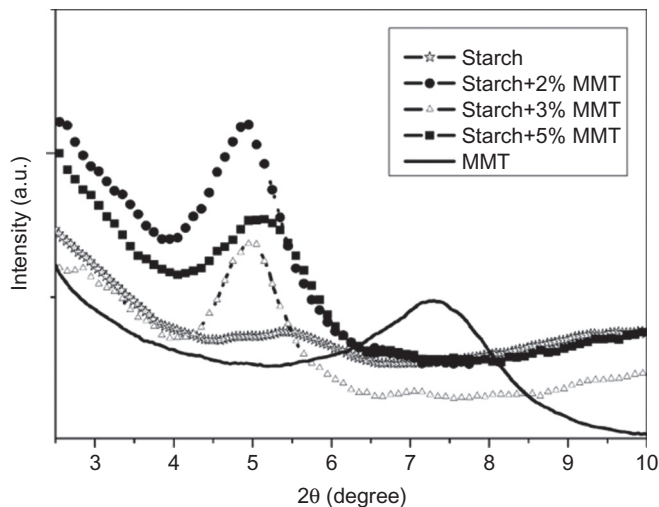


FIGURE 16.8

XRD patterns for potato starch, montmorillonite, and their nanocomposites.

From Cyras et al., 2008.

et al. (2008) and *Tang et al.* (2008) obtained similar results when they conducted x-ray diffraction studies on starch/montmorillonite composites; however, they came to the opposite conclusion that the presence of low angles (4.9°) corresponding to a 001 diffraction peak value of 18 Å suggest that the plasticizer (e.g., glycerol) is intercalated but no or few starch chains are intercalated into the MMT–Na layers. There is an ongoing dispute on this topic.

Transmission electron microscopy technology is another method for determining how well a nanoclay disperses into the starch matrix. It allows people to directly observe the nanoclay in the starch matrix. *Figure 16.9* shows TEM images of starch/MMT composites. *Figure 16.9a* presents a well-dispersed exfoliated structure, while *Figure 16.9b* shows poorly dispersed clay aggregates (*Mondragon et al., 2008*). The different nanoclays can be classified depending on their aspect ratio and geometry, such as layered particles (e.g., clay), spherical particles (e.g., silica), or acicular particles (e.g., whiskers, carbon nanotubes) (*Chivrac et al., 2009*). MMT is the most commonly used nanofiller among the nanoclays, because it is environmentally friendly and readily available in large quantities at relatively low cost (*Cyras et al., 2008*). Typically, MMT particles are thin, flat disks about 1 to 3 nm thick and 500 nm wide. It is composed of aluminosilicate layers stacked one above the other. The layers are loosely held together by very weak oxygen-to-oxygen and cation-to-oxygen bonds. Hence, water molecules and various ions are attracted into the interlayer space, causing expansion of the crystal (*Zhao et al., 2010*).

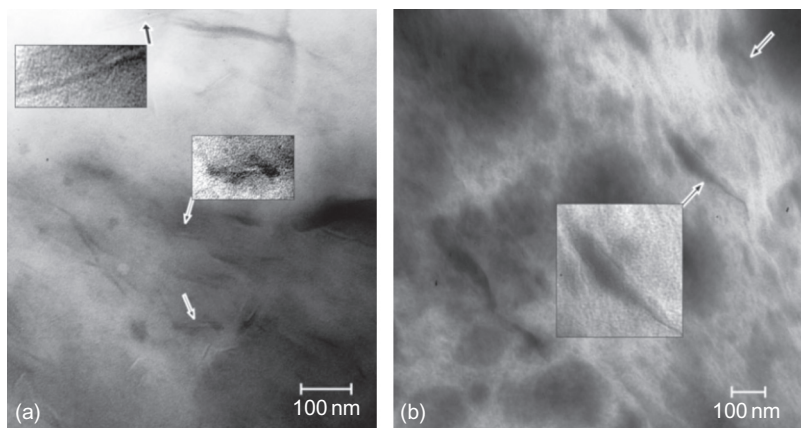


FIGURE 16.9

TEM images of (a) starch/nanoclay (2% level) nanocomposite, and (b) starch/nanoclay (5% level) nanocomposite.

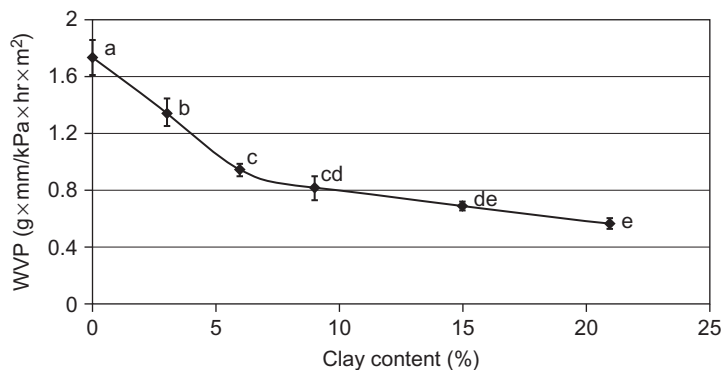
From Mondragon et al., 2008.

It has been reported that TPS/nanoclay nanocomposites have marked improvements in TS, gas barrier properties, and thermal and oxidative stability (Chivrac et al., 2010; Huang et al., 2004; Rhim and Ng, 2007). Huang et al. (2004) found that the addition of sodium montmorillonite increased tensile stress from 6 to 27.34 MPa, increased elastic modulus from 38.15 to 206.74 MPa, and decreased tensile strain from 85.32 to 16.82%. Moreover, Huang et al. (2006) achieved very high tensile stress and strain, 23.7 MPa and 158.9%, respectively, for cornstarch/MMT nanocomposites with formamide and urea added as plasticizers. Park et al. (2003) achieved similar improvements when they studied starch/MMT nanocomposites. The addition of 5% sodium montmorillonite increased TS from 2.6 to 3.3 MPa, E from 47 to 57%, and temperature at which the composite lost 50% mass from 305 to 336°C. Table 16.4 summarizes the effect of some nanoclays on the mechanical properties of TPS. In addition, nanoclay was found to improve moisture barrier properties. Figure 16.10 shows the effect of 0 to 21% MMT on the WVP of wheat starch/nanoclay composite films (Tang et al., 2008). WVP decreased as clay content increased, indicating that the WVP of wheat starch with 21% clay was 0.57 g mm/kPa•h•m², which was ≈ 70% lower than the WVP of the wheat starch blank. Cyrus et al. (2008) tested the effect of MMT on the water absorption rate, the effective diffusion coefficient (D_{eff}). They found that the D_{eff} decreased from 2.00 to 1.73×10^8 mm²/s when the MMT increased from 0 to 5%. Rhim and Ng (2007) postulated that nanoparticles dispersed in a starch matrix provide a tortuous path for water and gas molecules to pass through. This increases the effective path length for diffusion, thereby improving the barrier properties.

Table 16.4 Tensile Properties of TPS/Nanoclay Composites

Blend Composition	TS (MPa)	E (%)	EM (MPa)	References
100% TPS	2.61	47.0	—	Park et al. (2003)
97.5% TPS/2.5% nanoclay	2.79	48.9	—	Park et al. (2003)
95% TPS/5% nanoclay	3.32	57.2	—	Park et al. (2003)
90% TPS/10% nanoclay	3.20	52.0	—	Park et al. (2003)
100% TPS	11.82	4.62	840	Chung et al. (2010)
TPS/MMT	15.49	4.34	1390	Chung et al. (2010)
100% TPS	2.24	31.7	28.3	Chivrac et al. (2010)
97% TPS/3% MMT	2.32	27.3	35.6	Chivrac et al. (2010)
94% TPS/6% MMT	1.90	21.0	39.2	Chivrac et al. (2010)
97% TPS/3% SEP	2.91	36.5	45.3	Chivrac et al. (2010)
94% TPS/6% SEP	2.99	31.0	67.3	Chivrac et al. (2010)
100% TPS	2.65	34	18.5	Lu et al. (2012)
97% TPS/3% vermiculite	3.28	28	23.3	Lu et al. (2012)
110% TPS	1.5	33.5	8	Aouada et al. (2011)
99% TPS + 1% MMT	2.0	31.2	6.7	Aouada et al. (2011)
98% TPS + 2% MMT	2.3	40.1	11.4	Aouada et al. (2011)
97% TPS + 3% MMT	2.4	36.1	15.3	Aouada et al. (2011)
95% TPS + 5% MMT	2.8	37.8	23.8	Aouada et al. (2011)

Abbreviations: E, elongation at break; EM, elastic modulus; MMT, montmorillonite; SEP, natural sepiolite; TPS, thermoplastic starch; TS, tensile strength.

**FIGURE 16.10**

Water vapor permeability (WVP) of wheat starch-based nanocomposite films decreases with increasing MMT content from 0 to 21%. Error bars indicate standard deviation. Data points with different letters imply significant difference ($p < 0.05$).

From Tang et al., 2008.

Fiber

Fiber has been reported to enhance the mechanical properties, gas barrier properties, water resistance, and thermal stability of TPS (Gilfillan et al., 2012; Lu et al., 2012; 2009; Ma et al., 2005; Panthapulakkal et al., 2006; Prachayawarakorn et al., 2010). The improved mechanical properties were attributed to the strong bonding between the fiber and the starch matrix, resulting in good stress transfer. Gilfillan et al. (2012) reported that 5% addition of fiber increased the EM by 24% and TS by 16%; however, when the addition of fiber was greater than 5%, the TS decreased due to agglomeration of the fiber. Similar results were reported by other researchers. Mondragon et al. (2008) indicated that the TS of TPS increased from 2.5 to 7.7 MPa when fiber content increased from 0% to 20% (w/w). Ma et al. (2005) reported that an increase in fiber content from 0% to 20% (w/w) greatly increased the TS of a TPS composite up to 15.2 MPa. Regarding moisture resistance, it was reported that the addition of fiber slightly improved the TPS film's resistance to taking up moisture (Gilfillan et al., 2012; Prachayawarakorn et al., 2010). They suggested that this was due to the less hydrophilic character of the fiber. Zhang et al. (2011), however, found the opposite—that moisture content increased slightly with an increase in fiber content. Interestingly, they also found that fiber had the potential to enhance the TPS surface tension, leading to improved wettability of the TPS surface. Commonly used reinforcing fibers include cellulose nanocrystallites (Alvarez et al., 2005; Curvelo et al., 2001; Lu et al., 2006; Ma et al., 2005; Muller et al., 2009a,b; Soykeabkaew et al., 2004) and commercial regenerated cellulose fibers (Funke et al., 1998; Muller et al., 2009b).

Polymer

Another approach to mitigate TPS shortcomings is related to its hydrophilic characters and mechanical properties and involves blending starch with nonbiodegradable polymers such as low-density polyethylene (LDPE) (Girija and Sailaja, 2006; Ning et al., 2007; Wang et al., 2004a), high-density polyethylene (HDPE) (Huneault and Li, 2012), or biodegradable polymers such as polyvinyl alcohol (PVA), polyethylene oxide (PEO), polylactide, polycaprolactone (PCLP), polypropylene carbonate, polylactic acid (PLA), poly-3-hydroxybutyrate (Godbole et al., 2003; Ke and Sun, 2000; Luo et al., 2012; Preechawong et al., 2005; Wang et al., 2008; Yu et al., 2013), or polyester (Huneault and Li, 2012). Huneault and Li (2012) examined the properties of blends of TPS with high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polylactic acid (PLA), and polycaprolactone (PCL). Compared to TPS under ambient conditions, tensile properties such as EM and TS were enhanced. They also reported that a TPS/PE blend with maleic anhydride was able to extend up to 800%. Pushpadass et al. (2010) reported that starch/polyethylene, starch/polyvinyl alcohol, and starch/polyglycolic acid copolymers have enhanced mechanical properties.

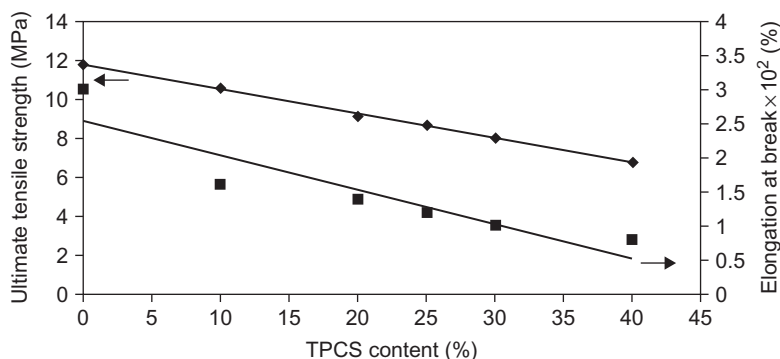


FIGURE 16.11

Tensile strength and elongation at break of the LDPE/starch blends decrease with increasing starch concentration in the composites.

From Sabetzadeh et al., 2012.

In spite of improvements in the mechanical properties, three major issues with TPS composites, particularly starch/LDPE films, are still present: (1) poor adhesion and compatibility between the hydrophilic starch and the hydrophobic synthetic polymer, which results in weak functional properties; (2) their nonbiodegradability; and (3) minor amounts of starch in the total composite ($\leq 40\%$) (Pushpadass et al., 2010). Wang et al. (2004b) studied rice starch/LDPE blends and reported that increases in rice starch content from 0% to 30% resulted in decreased TS from 14 MPa to 7.5 MPa and decreased E from 750% to 30%. Sabetzadeh et al. (2012) found similar results when they studied corn starch/LDPE blends. They reported that there was a continuous decrease in TS and a reduction in E when the corn starch concentration was increased from 0% to 40% in the corn starch/LDPE blends (Figure 16.11). This phenomenon was attributed to the incompatibility of starch and LDPE. Morphology studies of starch/LDPE blends using scanning electron microscopy (SEM) found that starch particles agglomerated in the LDPE matrix due to the high interfacial tension between the nonpolar PE and the highly polar starch (Abdul Majid et al., 2009) (Figure 16.12). One alternative has been investigated to overcome this problem: incorporating chemical compatibilizers into the starch/PE blends. Sailaja and Chanda (2001), Wang et al. (2004b), Abdul Majid et al. (2009), and Sabetzadeh et al. (2012) reported that the introduction of polyethylene-grafted maleic anhydride (PE-g-MA) improved miscibility between PE and starch and led to enhancement of the mechanical properties. Figure 16.13 shows how PE-g-MA improved the TS and E of the starch/PE blends. Such findings have been attributed to the fact that PE-g-MA improves the dispersion of starch particles and interfacial adhesion between the starch and PE phases. Sabetzadeh et al. (2012) further suggested that starch/PE blends containing 25 wt% corn starch would offer the required properties for PE packaging products.

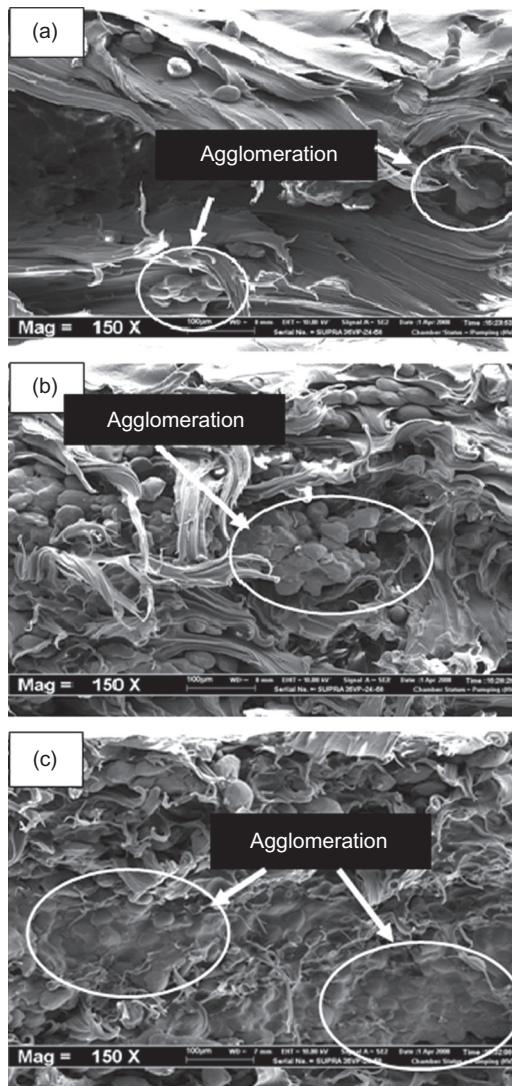


FIGURE 16.12

SEM surface micrographs of LDPE/TPSS blends: (a) 10 wt%, (b) 30 wt%, and (c) 50 wt% sago starch loading.

From Abdul Majid et al., 2009.

Besides the addition of compatibilizers, modification of starch is another alternative to improve the compatibility between starch and synthetic polymers in blends. [Stagner et al. \(2012\)](#) studied a blend of maleated thermoplastic starch (MTPS) and polybutylene adipate-*co*-terephthalate (PBAT). They noted that the

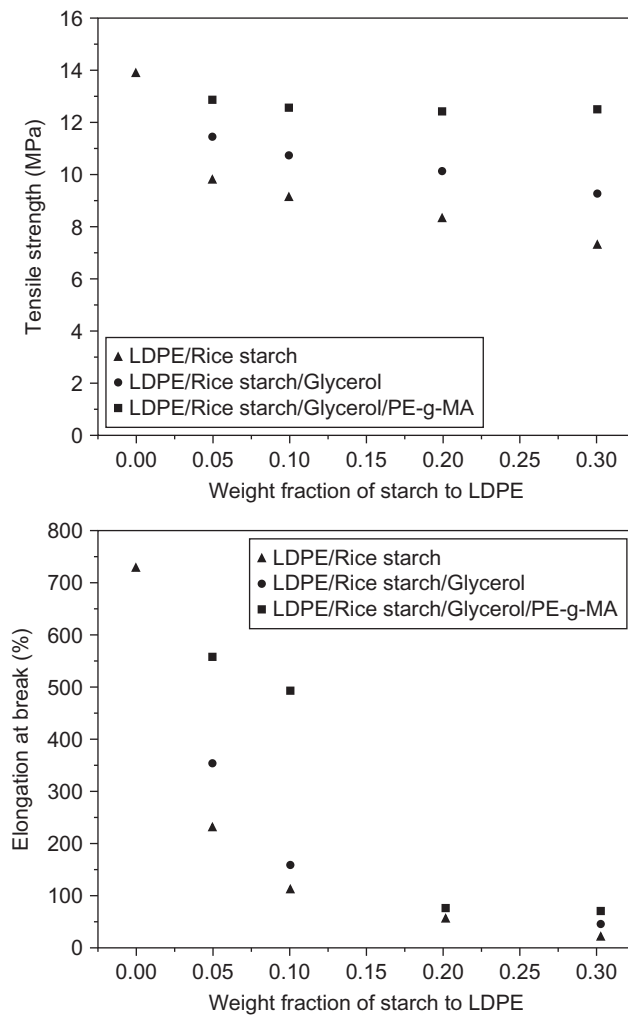


FIGURE 16.13

Tensile properties of LDPE/rice starch blends, LDPE/rice starch/glycerol blends, and LDPE/rice starch/glycerol/PE-g-MA blends, indicating that compatibilized starch/PE composite samples had higher tensile strength and elongation at break.

From Wang et al., 2004b.

values for the TS and E of films containing 20% MTPS were 17 MPa and 900%, respectively, greater than those of films containing 50% poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), 30% PBAT, 12% high-amylose corn starch, and 8% glycerol, which exhibited tensile strength and elongation values of 15 MPa and 368%, respectively. As well, [Stagner et al. \(2012\)](#) compared the TS and E of

modified TPS/PBAT with those of unmodified TPS/PBAT reported by other researchers and concluded that modified TPS/PBAT exhibited a stronger and more flexible mechanical nature.

CONCLUSION

Thermoplastic starch has promising potential for large-scale production of biodegradable packaging materials; however, its low mechanical properties and poor moisture vapor resistance are still big challenges for TPS products. Addition of nanoclays, polymers, plasticizers, fibers, addition of fatty acids (Jimenez et al., 2012) and organic acids (Olivato et al., 2012) and other methods, such as chemical modification of starch, have been utilized to improve TPS properties. These improvements of the mechanical and barrier properties of TPS products should satisfy industry needs.

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